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NEW PROCESS FOR CONTROLLING MERCURY VAPOR

BY

MERLE RANDALL AND H. B. HUMPHREY

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UNITED STATES DEPARTMENT OF THE INTERIOR - BUREAU OF MINES

NEW PROCESS FOR CONTROLLING MERCURY VAPOR[1/]

By Merle Randall[2/] and H. B. Humphrey[3/]

INTRODUCTION

Application of a new chemical spray in a mercury mine in which ore rich in native metal was causing salivation among the miners has given such favorable results that it is believed the process will be useful in other mines and perhaps in some plants where similar conditions exist. The process was originated by Merle Randall, professor of chemistry at the University of California.

GENERAL PROBELM

The presence of native quicksilver in mines from which the metal is produced has long been a source of trouble and danger to the workers. Men have been sickened and some of them have been disabled by exposure to the vapors present (even in workings that were well-ventilated by ordinary standards) and to contact with dust, dirt, and moisture with which the finely divided quicksilver was mixed. Where the ore was rich and this exposure was considerable men were able to work only a few days or weeks; where the exposure was less they were weakened and subject to ailments often attributed to other causes.

Many remedies were tried. One was to import new labor as fast as the men were disabled or left the job; another was to rotate the men between surface and underground employment; and still another was to require frequent changes of clothing and daily cleansing of the entire body and to prohibit smoking or eating underground. Some of these steps were effective where the native quicksilver was not too highly concentrated. Adequate ventilation also proved to be an important factor.

1/ The Bureau of Mines will welcome reprinting of this paper, provided the following footnote acknowledgment is used: "Reprinted from Bureau of Mines Information Circular 7206."

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In his study of mercury-vapor hazards in petroleum laboratories McCarroll (1)[4/] states:

> The absorption and retention of mercury vapor and dusts by the human body are recognized as definite health hazards, and *** industrial exposure generally is more severe and is accompanied by a higher incidence of chronic mercurialism than is experienced by laboratory workers.
>
> Under general conditions prevalent in laboratories, the possible hazard from inhaling mercury-impregnated dusts or compounds of mercury in the form of finely divided dust particles, from absorbing mercury or its compounds through the skin, or from affording it entrance into the body through the gastrointestinal tract is slight in comparison to that of inhaling metallic-mercury vapor. However, where compounds of mercury (especially the mercuric compounds because of their ready solubility) are present, metallic-mercury vapor could become secondary as a cause of mercurialism.

In discussing the cause of mercury poisoning, Sayers (2) states:

> The immediate cause of industrial mercurial poisoning is the absorption and retention of small quantities of the metal or one of its many compounds for an extended period of time. The absorption of 0.001 gram of mercury a day over an extended period is said to cause the disease.
>
> Quicksilver may enter the body through the skin, the gastrointestinal tract, or the respiratory tract. When applied to the skin it is more rapidly absorbed if the person is perspiring or if the mercury is impure or dirty. Dry and clean mercury on a dry clean skin is probably absorbed only with difficulty.
>
> Although comparatively large quantities of the metallic mercury can be taken in at one time by mouth without causing death, small quantities often repeated will lead to chronic poisoning from absorption and accumulation in the body tissues. Metallic mercury vaporizes at low temperatures, vaporization being noticeable at a temperature as low as 8.5° F., the amount vaporized increasing with the temperature. The vapors, fumes, and dust enter the body by all three portals of entry, as they

4/ Numbers in parentheses refer to items in the bibliography.

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settle on the clothing or skin, are breathed into the lungs, or are swallowed with food or other substances taken into the mouth.

Mercury volatilization is described by Henderson and Haggard (3) with the statement that:

> Mercury evaporates even at ordinary temperatures, and the concentration reached by the vapor in the air depends on the temperature, the extent of surface exposed, and the rate of air exchange in ventilation. In still air, the heavy vapor tends to collect close to the surface of the exposed metallic mercury and thus inhibits further volatilization. Where the air is moved by ventilation a greater rate of volatilization is attained, but insufficient time is allowed for the air to reach more than partial saturation with the mercury. Temperature has an important practical bearing, inasmuch as the rapidity of volatilization and the equilibrium concentration both increase greatly with rise of temperature.
>
> The rate of volatilization of mercury at any temperature *** varies proportionally with the surface exposed. This has a practical bearing because of the difference of the behavior of mercury in various states of purity. Clean mercury is readily divided into globules, but these globules coalesce when brought together again. On the other hand, mercury soiled by grease and dust is prone to divide into minute globules, which do not coalesce. *** The greater the subdivision, the larger is the surface presented for volatilization. In this manner a comparatively small amount of mercury in an almost or quite invisible state of subdivision may present an exposed surface equivalent to that of a large mass of mercury coalesced in a dish or pan. The vapor has neither taste nor odor to give warning of its presence.

TOXIC LIMITS

Various threshold limits have been given by authorities (see references 3 to 7 in bibliography) for the concentration of mercury in the air that would be hazardous to health. A limit of 0.15 milligram per cubic meter was adopted by the California Industrial Hygiene Service and the Industrial Accident Commission as an average between the 0.2-milligram limit specified by some authorities and the 0.1 settled upon by others. This was done because of the indications that all effects of low concentrations had not been determined fully.

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HISTORY OF LOCAL OCCURRENCE

Stories are told of terrible conditions in some of the California mines in early days, and it is probable that these are at least based upon facts, although certainly exaggerated as to details. It is a matter of record that a number of cases of salivation occurred underground in the mines working in 1939 and 1940. These cases were few compared with those resulting from faulty practices and equipment in the reduction plants, mainly because native quicksilver was present in only three of the mines and in very small quantities.

Three early mines in California in which native quicksilver caused salivation were the Almaden, Oceanic, and Socrates. Native quicksilver has also been reported in the ore from the following mines: Dawson and Kings in Kings County; Baker, Big Injin, Chicago, Mirabel, Helen, and Wall Street in Lake County; Petriquin and Gillette in Monterey County; La Joya in Napa County; Red Hill in Orange County; Rinconada in San Luis Obispo County; Great Northern in Siskiyou County; and Culver Baer, Covun Point, Hope, and Rattlesnake in Sonoma County.

There may have been unrecorded occurrences of native quicksilver in other mines. Some of these were being reopened in 1940 or 1941.

DESCRIPTION OF PROBLEM AT THE CONTACT MINE

The Contact mine in Sonoma County was put into random production from 1932 to 1936 and then changed hands, and a small amount of metal was produced in 1938. In 1940 the mine again changed hands. Like the nearby Socrates mine, the ore carries cinnabar and native quicksilver and occurs along a serpentine and sandstone contact that dips steeply to the east into a mountainside. The ore shoot is in the form of an irregular pipe raking to the south on the dip.

In June 1940 the mine was being developed through a small inclined shaft divided into a skip compartment and a ladderway. The shaft was sunk to the 200-foot level, and drifts were opened on the 100-, 150-, and 200-foot levels. A winze was being sunk in the ore shoot, and a raise had been started in the ore. Determinations of the mercury-vapor concentration at these adjacent points were made by a party comprising representatives of the California Industrial Accident Commission, the California Industrial Hygiene Service, and the Bureau of Mines, who were surveying the health and accident hazards in the mercury mines of the State. The results of these tests showed that a serious hazard existed, and later experience with men working in the ore confirmed this. (See table 2, column marked 6/19/40, for concentrations found.)

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Owing to the suspension of mining during a change of management and erection of a new furnace no action was taken by the State until a second series of tests (April 22, 1941) confirmed the original findings. Some improvements in ventilation were made, and other tests (May 8, 1941) followed. The management cooperated with the Industrial Accident Commission and the insurance carriers by increasing ventilation, protecting miners with heavy rubber clothing and gloves, providing means and service for frequent washing and changing of clothes, installing sprays on the drills, and prohibiting smoking and eating underground. These measures certainly reduced the severity of the salivation, which apparently affected most of the miners working in the ore, so that although numerous cases were reported none seemed to be serious.

It was evident that measures had to be taken to reduce the mercury-vapor concentration in the active portions of the mine from about 1.7 milligrams per cubic meter to below the specified limits of 0.1 to 0.2 milligram. The recommendation was made that a dual system of ventilation, using both exhaust and blowing ducts, be installed from the outside to the working points, with the expectation that the mercury vapors at these points might be replaced continuously by fresh air.

PRESENTATION OF PROBLEM TO PROFESSOR RANDALL

The management was hopeful that a less costly and elaborate method of combatting the difficulty might be found and laid the problem before Prof. Merle Randall of the Chemistry Department of the University of California. It was thought that by increasing the ventilation in the mine movement of air over the surface of small globules or droplets of mercury would be increased and the rate of evaporation of the mercury would be increased in much the same manner that the rate of evaporation of water from a wetted surface is increased by an increased movement of unsaturated air over its surface. The concentration of mercury vapor can, of course, be decreased to some extent by increased ventilation, but it was believed that the cost of increasing ventilation enough to reduce the mercury-vapor concentration below the desired limit of 0.15 milligram per cubic meter would be too great, and adequate volume might even be unattainable.

On the other hand, if all the droplets of liquid mercury were covered with a film, the rate of evaporation probably would be reduced greatly and a moderate volume of ventilation - enough for the comfort of the miners - would be ample to reduce the mercury-vapor concentration to safe limits.

Quoting from General Electric Quarterly 104, McCarroll (8) states that the rate of diffusion of mercury vapor through even a thin film of water is very slow. The possibility of using water vapor to form a film

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was discarded, because even a moderately rapid flow of air unsaturated by water vapor over a surface quickly evaporates a water film, and a saturated atmosphere that would not dry the water film would be uncomfortable for the miners and would greatly decrease their efficiency.

Stock (U. S. Patent 1,984,164, December 11, 1930) proposed to cover exposed mercury surfaces with an active carbon impregnated with a halogen.

As the mine waters of the Contact mine were slightly alkaline, it was possible to use alkaline polysulfides without danger of producing poisonous hydrogen sulfide gas. The faces, muck piles, walls, timbers, stopes, tunnels, and other parts of the mine were sprayed with a dilute solution of calcium polysulfide. The sulfide film reacted with the metallic mercury, diffusing through the film of alkaline polysulfide in contact with the droplets. Calcium polysulfide is the most readily available of the polysulfides, and when certain agents are added it is not irritating to those working with it.

A liquid spreader of the emulsified-oil type is very effective in spreading the alkaline polysulfide film over all the mercury droplets. Also, a fungicide adhesive with a petroleum-oil base assists in the formation of a durable film and greatly reduces the caustic effect of the lime-sulfur solution. Finally, wettable sulfur is added to the spray mixture to give a color that will assist the operator in spotting areas not previously covered. A preferred formula is given in the following table:

TABLE 1. - Formula for spray mixture for treating mines having free quicksilver

Lime-sulfur, 29 percent calcium polysulfide, 31° B.	gal.	2.5
"Ortho" liquid spreader	pint	1
"Ortho" fungicide adhesive	gal.	1
"Flotox" wettable sulfur	lb.	5
Water	gal.	100

The various ingredients listed in table 1 are furnished by the California Spray-Chemical Corporation of Richmond, Calif. The quantities given suffice to make approximately 100 gallons of spray mixture. In the tests at the Contact mine, the ingredients were mixed in a small, portable spraying machine and applied by the technique usually used for orchard lime-sulfur spraying solution. The spraying machine contained an agitator for continually mixing the contents of the tank. All spaces back of the timbering and the back as well as the exposed sides of the timbering were wetted. Approximately 98 percent of all exposed surfaces could be

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covered. The working faces and the roofs or backs of the stopes were sprayed. All unused parts of the mine were bratticed off.

After each blast, newly exposed faces and muck piles were wetted with the spray, and such parts of the mine as were exposed to the direct action of dust particles also were rewetted.

Owing to the strong blast of air from the drills, which tends to blow the surface of adjacent droplets clean, it is desirable to introduce small proportions of the spray mixture into the compressed-air lines for operating the drills and also into the water supplied for keeping the drill hole free. This is easily done by using an air-line "lubricator" containing the spray solution.

In a preliminary test of this process in one section of the mine, the concentration of mercury vapor before treatment was approximately 1.8 milligrams per cubic meter. After treatment for 8 hours, the selenium sulfide paper exposed in the General Electric mercury-vapor test lamp was only slightly darkened, indicating the presence of less than 0.1 milligram of mercury per cubic meter.

This treatment is also applicable to semiclosed rooms, such as those used for the recovery of sponge gold from amalgams, kiln or furnace rooms, condenser buildings, clean-up tables, mercury boiler buildings, and laboratories where mercury is likely to be spilled.

THE CHEMICALS

Lime-sulfur solution. - Calcium polysulfide or lime-sulfur solution is sold by many manufacturers. It should contain preferably more than 29 percent of calcium polysulfide and have a density of 31° to 33° B. The solution should be completely saturated with sulfur so that the wettable sulfur will not be dissolved. Under these conditions, considerable calcium pentasulfide will be present.

Liquid spreader. - "Ortho" liquid spreader manufactured by the California Spray-Chemical Corporation of Richmond, Calif., is made, by the process described by Volck (U. S. Patent No. 1,922,607, Aug. 15, 1933), of casein ammonia soap and cresylic acid. The product is an organic sulfur acid component from relatively heavy mineral oils and is produced by the reaction of these oils with sulfuric acid at a controlled temperature. This spreader proved very satisfactory. Other suitable spreaders or wetting agents that have the property of causing the spray to penetrate readily and to adhere as a film rather than in drops may be used.

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Fungicide adhesive. - "Ortho" fungicide adhesive, also manufactured by the California Spray-Chemical Corporation, has a petroleum base containing emulsified oils of the light lubricating class. Its purpose is to provide a film-forming ingredient, more or less unaffected by water, that will maintain the polysulfide constituent in the film for a considerable time, thus effectively sealing the mercury droplets within a protective absorbent layer. The adhesive also materially reduces the possibility of any caustic effect of the polysulfide solution on the operators. The lubricating oil in the adhesive also is effective in passing the solution through the drills.

Wettable sulfur. - "Flotox" wettable sulfur, also manufactured by the California Spray-Chemical Corporation, greatly assists the operators to distinguish the parts that have been sprayed before. A dye may be used, but the wettable sulfur has the additional advantage of maintaining a very slight vapor pressure of sulfur.

LATER SAMPLING

After the treatment had been applied for several weeks and tests with the General Electric mercury-vapor lamp by mine officials showed favorable results, the survey party returned and repeated the procedure of sampling and testing used previously. These results confirmed the predictions made for the treatment and indicated a mercury-vapor concentration of between 0.1 and 0.2 milligram per cubic meter.

Table 2 lists the samples and the results of sampling on various dates. The Greenburg-Smith impinger was used to collect samples of dust that would carry a small amount of mercury, and the General Electric selenium sulfide lamp was used to determine the amount of mercury vapor in the air.

CONCLUSION

A new chemical-spraying process for controlling mercury vapor in mines and other closed and semiclosed spaces has proved effective in reducing the mercury-vapor concentration enough to remove any serious health hazard provided that "good housekeeping" is maintained and the spray covers all exposed mercury droplets and dust. With the reduction of the health hazard in mines containing free quicksilver, many properties heretofore unprofitable for operation may be reopened. Also, similar problems in other processes in which mercury is used may be solved.

The process described is the property of Merle Randall, of 2512 Etna Street, Berkeley, Calif. (serial 399,417, filed with the United States Patent Office, June 23, 1941), to whom inquiries regarding license for its use should be addressed.

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TABLE 2. - Results of sampling in Contact Mine.

Sampling place	Milligrams per cubic meter				
	Before treatment			After treatment	
	6/19/40	4/22/41	5/8/41	5/27/41	6/9/41
Main shaft, 100-foot level					0.08
150-foot stope, mucking and drilling (light)					.00
200-foot level, tramming	1.25				.08
250-foot level, after blasting		1.77		0.16	.16
250-foot level, drilling	1.70				.13
200-foot stope, drilling		1.25			
200-foot stope, not working			0.99		
250-foot stope, drilling			1.65	.10	
250-foot stope, 3 hours after blast		1.67			
320-foot level in winze, varied work (not in ore)					.00

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